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Potential Exposure to Dislodgable Residues after Application of Two Formulations of Methyl Parathion to Apple Trees

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The acute poisoning of workers who have entered crops too soon after application of pesticides has been documented in a number of areas of the United States, but is a particular problem in California (GUNTHER et al. 1977). For this reason, the introduction of particularly toxic new pesticides which will be used in such a manner as to provide the opportunity for reentry exposures should be preceded by studies to determine safe reentry intervals. Similar studies should precede the introduction of novel formulations which may significantly affect reentry exposure.

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Potential Exposure to Dislodgable Residues after Application of Two Formulations of Methyl Parathion to Apple Trees

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The acute poisoning of workers who have entered crops too soon after application of pesticides has been documented in a number of areas of the United States, but is a particular problem in California (GUNTHER et al. 1977). For this reason, the introduction of particularly toxic new pesticides which will be used in such a manner as to provide the opportunity for reentry exposures should be preceded by studies to determine safe reentry intervals. Similar studies should precede the introduction of novel formulations which may significantly affect reentry exposure.

One method that has been suggested for the determination of safe reentry intervals involves the determination of dislodgable residue levels that will not result in significant cholinesterase depression (KAHN 1979). However, cholinesterase depression is not a satisfactory indicator of exposure in many instances. Not all pesticides are cholinesterase inhibitors and it is possible that some exposure will result in deleterious biological effects at levels of exposure lower than those necessary to elicit cholinesterase depression. DAVIES and COWORKERS (1979) have demonstrated that urinary metabolites of pesticides may be more sensitive indicators of exposure than biologic or environmental indices. However, methodology is not currently available for sensitive detection of urinary metabolites from all pesticides.

Another approach to establishment of safe reentry intervals is correlation of dislodgable residues to potential exposure, which is determined by direct methods. These direct methods involve the entrapment of toxic material as it comes in contact with a workman or removal of retained toxicant at the end of the exposure period (WOLFE et al. 1967). Direct methods only provide the potential for exposure since information about absorption is necessary to determine actual exposure. Nevertheless, as information becomes available concerning the relationship of potential exposure to biological effects, a correlation of dislodgable residue levels to potential exposure should allow the establishment of safe reentry intervals by the relatively simple analysis of pesticide residues. An example of a study which relates potential exposure to biological effect is that of SPEAR and COWORKERS (1977), who demonstrated a good correlation between dermal exposure to foliar paraoxon residues and cholinesterase inhibition.

The dislodgable residues chosen for the present study

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resulted from application of microencapsulated (M.E.) or emulsifiable concentrate (E.C.) methyl parathion (O,O-dimethyl O,p-nitrophenyl phosphorothioate). Presumably the differences in these two formulations would provide quite different residue characteristics, which would result in large differences in both dislodgable residue levels and potential exposure. If a correlation could be established between the dislodgable residues and potential exposures for these very different formulations, then this would provide excellent evidence that the proposed approach for setting safe reentry intervals was plausible.

Respiratory and hand exposures were determined under conditions designed to result in maximum contact with and disturbance of residues on apple foliage after spraying with M.E. or E.C. formulations of methyl parathion. These exposures were examined to determine if they could be correlated to levels of dislodgable residue remaining at from one to seven days after spraying. Dislodgable residue persistence was determined for both formulations.

MATERIALS AND METHODS

Three airblast applications were made to apple trees at intervals of approximately one month. An equivalent amount of active ingredient (A.I.) was applied for either formulation. The amount applied was 1.68 Kg A.I./ha (1.5 lb /A) in 3,740 L (400 gal) of water. The trees were Sharp Red Delicious approximately five years old, which were small enough that a test subject could easily rub his hands over all the branches of one tree within one minute.

Two test subjects participated in the study. They wore light cotton gloves to measure hand exposure and modified dust respirators to assess respiratory exposure (DURHAM and WOLFE 1962). Both subjects obtained maximum exposure to the residues on three trees at each sampling period. The sampling periods were at one, two, three, and seven days after each of three sprayings. A 30 leaf-punch sample was taken from each of the three trees after which a subject would disturb the residues as much as possible by vigorously rubbing all the foliage on the three trees for a period of one minute per tree.

Dislodgable residues were extracted from the leaf-punch samples by the following modification of the procedure of IWATA et al. (1977). After dislodgment of foliage residue into a Sur-Ten solution, the residue was extracted by partitioning into two 50 mL portions of hexane. Foliage dislodgable residue levels were calculated using the surface area of both sides of the 22 mm (0.88 in) diameter leaf punches. Residues were Soxhlet extracted from gloves and respirator pads with toluene.

Sur-Ten solutions, cotton gloves, and respirator pads were fortified with simulated spray solutions and were then extracted in the same manner as the field samples to determine recoveries.

The simulated sprays were prepared using authentic spray concentrates and contained the same concentration of A.I. as the spray used on trees. Media were fortified with amounts of A.I. that were expected for the field samples. The simulated spray solutions were mixed continuously on magnetic stirrers while portions were being removed to fortify the media.

Extracts were analyzed using a gas chromatograph equipped with a flame photometric detector. A glass column, 1.83 m x 4 mm (inside diameter), packed with 1.5% OV-17/1.95% OV-210 on 80/100 mesh Gas Chrom Q was used with a nitrogen carrier gas flow of 55 mL/min. Inlet, column, transfer line, and detector temperatures were 210, 200, 220, and 220°C respectively.

RESULTS AND DISCUSSION

Recoveries from sampling media fortified with simulated sprays are shown in Table 1. Each recovery sample was replicated four times. Even though the recoveries of methyl parathion from Sur-Ten solutions, which were used to evaluate the dislodgable residue method, were very poor for the M.E. material, the small standard deviation obtained indicated that recoveries were reproducible. All values reported in the rest of this communication were corrected for the losses indicated by these recovery studies.

TABLE 1

Recovery of methyl parathion from fortified sampling media

Formulation	Amount of active ingredient added (µg)	Sample medium	% recovery
Emulsifiable concentrate	10	Sur-Ten solutions	100 ± 3
	50	Cotton gloves	81 ± 1
	10	Respirator pads	77 ± 1
Micro-encapsulated	10	Sur-Ten solutions	19 ± 1
	50	Cotton gloves	74 ± 3
	10	Respirator pads	94 ± 4

[a]Mean ± standard deviation for four replicates.

The persistence of dislodgable residues for the three sprayings are shown in Figure 1. These results are presented as the % of the initial residue remaining at the various sampling periods

because of the large variation in initial residue levels obtained. Initial E.C. residues (mean ± standard deviation) were 3.3 ± 0.9, 2.2 ± 0.1, and 1.6 ± 0.1 µg/cm^2. The initial M.E. residues were 3.1 ± 0.4, 4.1 ± 0.7, and 1.2 ± 0.1 µg/cm^2. Each of these initial values was obtained from 30-punch samples taken from each of six trees. No explanation can be made for the variation found. It occurred in spite of the fact that care was taken to prepare sprays containing equal amounts of active ingredient and to reproduce the tank mixes used for the three applications.

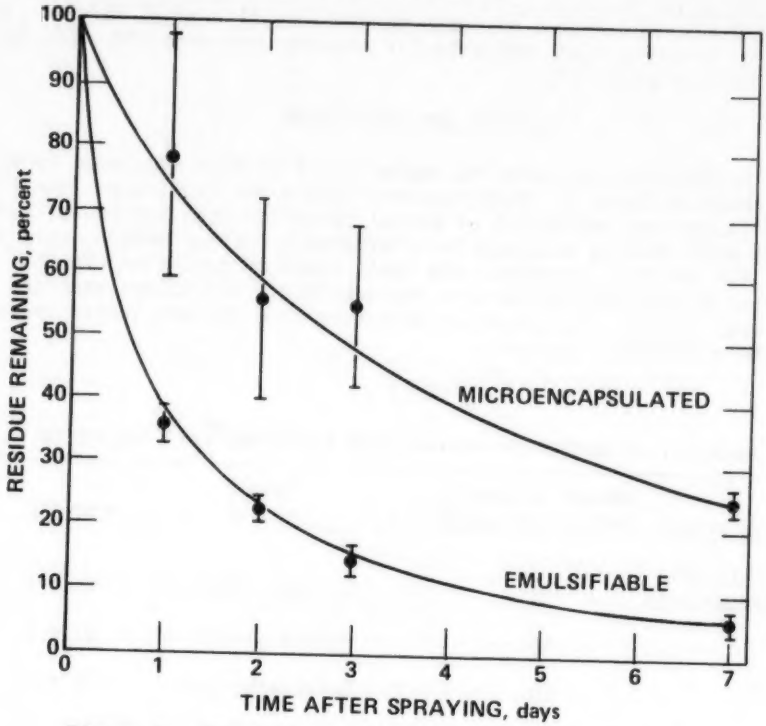


Figure 1. Persistence of dislodgable residues of methyl parathion on apple foliage. Bars indicate ± standard deviation for three replicates.

The use of the M.E. dislodgable residue data, in spite of the poor recoveries obtained, is supported by the results of WARE et al. (1973) and CARDARELLI (1976). WARE found a similar persistence as % of initial residue for M.E. methyl parathion applied to cotton in Arizona. CARDARELLI reported that E.C. formulations provide one to three days of residual control while an equivalent application of M.E. formulations provide five to eight days of control. The present study indicates that the residue at one day after

application of the E.C. formulation is approximately equal to the residue at five days after application of the M.E. formulation.

Residues recovered from cotton gloves and respirator pads are shown in Table 2. Since the study subjects attempted to obtain maximum exposure, the values found in this study must not be equated with those that would be received during actual apple thinning. However, the ratio of exposure to residues from the two formulations should be the same during actual thinning as during this simulated thinning.

TABLE 2

Hand and respiratory exposure to foliage residues

Formulation	Days after spraying	Exposure (µg)[a]	
		Hands	Respiratory
Emulsifiable concentrate	1	580 ± 420	2.1 ± 0.9
	2	330 ± 290	3.0 ± 1.2
	3	240 ± 200	2.1 ± 0.6
	7	55 ± 15	1.4 ± 0.4
Micro-encapsulated	1	3,100 ± 580	12 ± 2
	2	3,200 ± 200	9.3 ± 3.4
	3	3,000 ± 190	7.3 ± 4.4
	7	1,000 ± 790	5.0 ± 3.7

[a]Mean ± standard deviation for 6 determinations (two exposures after each of three sprayings).

These data indicate that assumptions about the relative reentry safety of residues based on LD_{50} data are prone to inaccuracy. The acute dermal toxicity of the M.E. formulation is reported to be approximately 1/20 that of the emulsifiable material (CARDARELLI 1976). Therefore, for crops sprayed with the M.E. material, it might be assumed that safe reentry could be allowed sooner than 48 h, which is the current legal reentry time for methyl parathion (ANONYMOUS 1974). However, the present study indicates approximately a tenfold higher potential for dermal exposure to the M.E. residues at 48 hours than for the residues from the E.C. formulation. This indicates that the potential for acute toxic effects due to dermal exposure to residues from the M.E. formulation would be 1/2, not 1/20, of that due to dermal exposure to residues from the E.C. formulation at 48 hours after spraying.

The maximum difference in potential for respiratory exposure

to the two types of residues occurred 24 hours after spraying. At that time, there was six times as much material collected on respirator pads worn while disturbing foliage treated with the M.E. formulation as with the E.C. formulation. Unfortunately, data comparing the respiratory toxicity of the two formulations is not available, so the significance of the sixfold greater potential respiratory exposure due to the M.E. material cannot be assessed.

Data were examined for linear correlation between the dislodgable residues from either formulation and potential exposure. The correlation coefficients for dislodgable residues, from application of the E.C. formulation, and hand or respiratory exposures were 0.873 and 0.342, respectively. For dislodgable residues from application of the M.E. formulation, these respective correlation coefficients were 0.700 and 0.787. These data indicated that even though removal of foliage residues with a detergent solution may be quite different from removing them by body contact, the dislodgable residue method produced a reasonably accurate estimate of the potential for dermal exposure at various times after spraying. It also gave a good estimate for potential respiratory exposure to residues from the M.E. formulation but not to residues from the emulsifiable formulation.

In summary, this study illustrated that simply comparing the acute dermal toxicities of two formulations of the same spray material may not be a valid procedure for establishing a reentry time for a new formulation. The effect the formulation will have on the ease with which residues can be transferred to workers must also be considered. The persistence of residues from the application of two formulations of methyl parathion was also determined. Finally, evidence was presented that supports the dislodgable residue method as a valid procedure for predicting the potential for dermal exposure to foliage residues.

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